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**“Tunable PhoXonic Band Gap Materials from Self-Assembly of
Block Copolymers and Colloidal Nanocrystals
(NBIT Phase II)”**

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14. ABSTRACT This collaborative Korea-USA proposal aims to design and fabricate tunable phoxonic band gap materials by self-assembly of block copolymer and/or colloidal crystals, characterize the resultant structures and finally measure and model/simulate their novel properties defined by their interaction with photons and phonons. Concerning this, we seek to develop methods and understanding to create both periodically structured materials (Bragg gap materials) and non-periodically structured materials (resonance gap materials). For that, self-assembly of block copolymers is chosen for creating a model system of tunable Bragg gap material, and self-assembly of colloidal crystals is for tunable resonance gap materials. This proposal brings a complete set of activities together to invent and exploit new periodic/non-periodic materials based on self-assembly systems.					
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Tunable PhoXonic Band Gap Materials from Self-Assembly of Block Copolymers and Colloidal Nanocrystals

Introduction

Controlling waves has long been a major research topic in the various fields of science and technology. In recent years, propagation of electromagnetic or elastic waves in so-called photonic and phononic crystals respectively has been of great interest due to their broad applications. Photonic crystals and phononic crystals can be used for isolating light and mechanical vibration respectively and are periodic composites made from, in the case of photonic crystals, high and low dielectric regions and in the case of phononic crystals, regions of high and low mechanical impedance.[1-3] By proper choice of materials and structural geometry, one can create gaps in the density of states for photons and phonons respectively as well as tailor the detailed dispersion relationship for waves propagating in the structure. Since the same basic ideas underpin both photonic and phononic crystals, it seems obvious to explore the possibility of making materials that exhibit both types of band gaps simultaneously (**PhoXonic** band gaps where $\mathbf{X} = \mathbf{t} + \mathbf{n}$).

Typically the formation of band gaps is explained by the Bragg scattering of photon or phonon by a periodic lattice; multiple interference effects by Bragg scattering create an energy gap along the Brillouin zone boundary. This explanation naturally requires the existence of the periodic lattice for the formation of band gaps, and therefore it has been widely believed that the lattice periodicity is indispensable for the band gap formation. Alternatively gaps can form if the scattering objects constituting a material have strong resonance states in the frequency range of interest. This model is an analogy of the tight-binding model in the formation of electronic band gaps in amorphous semiconductors (eg. *a*-Si and *a*-Ge). In this case, the band gap is independent of the structure. To be more specific, not even order or periodicity is required, if only a minimal nearest-neighbor distance (short-range order) is retained. Here we designate such non-periodic structures with a only short-range order as “*quasi-amorphous structures*”. This tight-binding model can be extended to quasi-amorphous structures for formation of photonic/phononic band gaps. Concerning the formation of 3D complete band gap, quasi-amorphous structures are advantageous because they are completely isotropic. In the case of crystalline materials, Bragg scattering is stronger along certain crystal axes, which makes the band gap anisotropic and often leads to only partial gaps along certain directions of the structure.

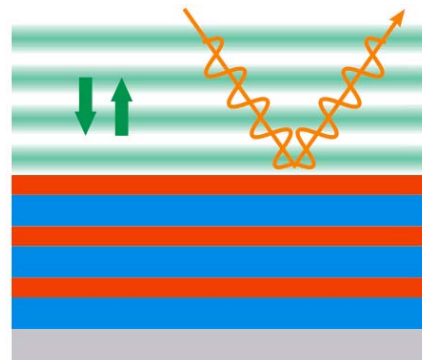


Figure 1. Sound and light waves are incident on the 1D tunable phoXonic crystals. As the waves have a frequency within the bandgap, propagation is not allowed and the waves are

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crystals, characterize the resultant structures and finally measure and model/simulate their novel properties defined by their interaction with photons and phonons. Concerning this, we seek to develop methods and understanding to create both periodically structured materials (Bragg gap materials) and non-periodically structured materials (resonance gap materials). For that, self-assembly of block copolymers is chosen for creating a model system of tunable Bragg gap material, and self-assembly of colloidal crystals is for tunable resonance gap materials. This proposal brings a complete set of activities together to invent and exploit new periodic/non-periodic materials based on self-assembly systems.

Proposed Research

The proposed research is organized into three complementary activities: Fabrication of Periodic and Non-Periodic Structures, Modeling and Simulation of Structures and Their Properties and Experimental Characterization of Structures & Defects and Properties. Overall, the aim of the research is to extend the reach of polymer physics into newly emerging areas of physics (photonics and phononics and their combination) to utilize the sensitivity of the propagation of waves in the individual component polymer domains to learn about polymer behavior in relatively small confined dimensions ($\sim 5\text{nm}$ to 1000nm) and to realize the unique advantages of polymers (processing, large response to a wide variety of stimuli) with hopes to actually demonstrate property performances that can elicit interest in potential technologies. Furthermore, we aim to elucidate dependency of optical and acoustic properties on their structures (periodic and non-periodic) and to find out fundamental parameters affecting them.

Fabrication of Periodic Structures via Self Assembly of Block Copolymers

The Thomas group has contributed substantially in the area of self assembled block copolymer structures, including block polymers (A/B and A/B/C; linear, star) homopolymer-block polymer blends and nanoparticle-block polymer blends. Utilizing their rich morphologies and periodicity dictated by molecular weights, one can create a variety of photonic/phononic structures. Since Bragg gap materials require highly ordered structures, there is high demand to have single crystal-like specimens with prescribed orientation. The large amount of on-going work in the polymer community for enabling structural control and long range order and orientation of microdomains, particularly in thin film geometry, is thus very valuable to us for the optimal use of BCP structures in 1D and 2D periodic structures.

Tuning of photonic structures is highly desirable. By incorporating gels, one can make polymeric systems versatile photonic/phononic materials responding to a wide variety of stimuli such as pressure, temperature, solvent, pH etc. For example the co-PIs of this proposal successfully developed a novel concept to combine the periodic nature of block polymers with the extreme responsiveness of a polyelectrolyte gel to produce a record reversible, subsecond response, $> 500\%$ shift in the stop band position ($\sim 300\text{nm}$ to 1600nm) via swelling/deswelling of the polyelectrolyte block in a 1D periodic lamellar

block polymer in contact with an aqueous solution with variable salt content (see figure 2).[4]

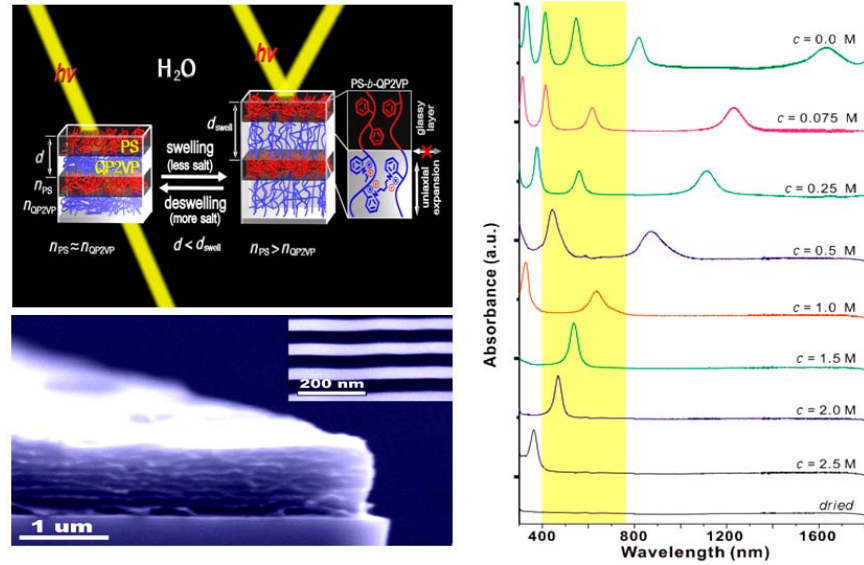


Figure 2. Structure of tunable photonic gel and its tunability. The fundamental band gap (peak 1) moves from the UV to the IR as the salt concentration in water is varied. Reference [4] (Nature Materials).

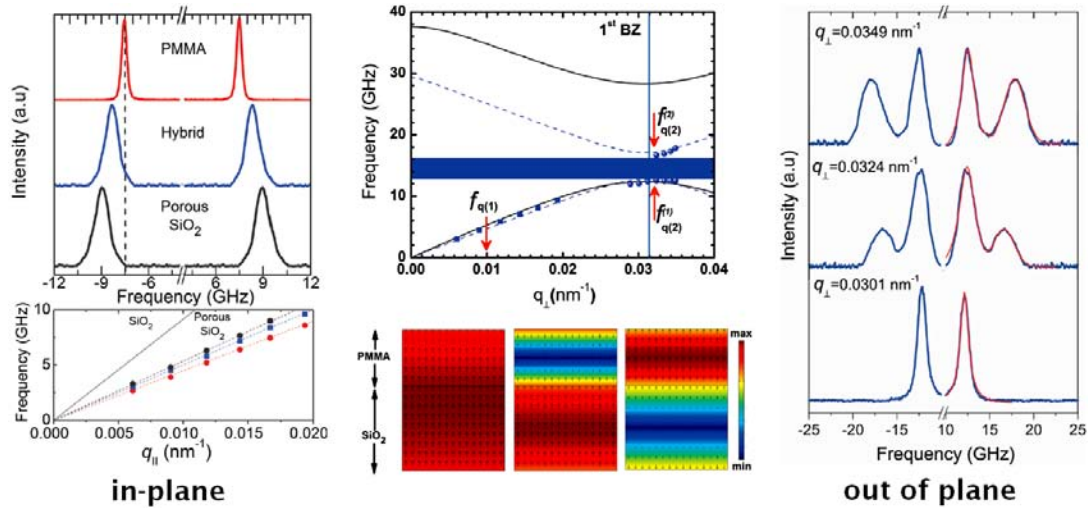


Figure 3. Experimental dispersion relation for phonon propagation along the direction of periodicity (middle). The highlighted blue region indicates the observed hypersonic band gap. BLS spectra for sound propagation parallel (left) and normal (right) to the surface. Reference [5] (Nano Letters).

The Thomas group has also demonstrated 1D hypersonic phononic crystals consisting of a multilayer stack of alternating SiO_2 and poly(methyl methacrylate) (PMMA) nanolayers

(see figure 3). By use of Brillouin light scattering (BLS), the dispersion relations were recorded for phonon propagation along the periodicity direction. The band gap to midgap ratio of 0.30 occurs for elastic wave propagation along the periodicity direction, whereas for inplane propagation, the system displays an effective medium behavior. The porosity in the silica layers presents a structural scaffold for the introduction of secondary active media for potential coupling between phonons and other excitations, such as photons and electrons.

In this part of work, we are going to explore the extreme tunability of polyelectrolyte gel embedded block copolymer structures to a variety of stimuli including pH, species of counter anions and electric fields. For that, we are going to use PS-*b*-P2VP block copolymers as a model system, utilizing the quite versatile chemistry of the P2VP blocks for modulating charge properties, dielectric properties, species of counter ions and cross-linking density which all sensitively affect optical/acoustic properties and hence tunability through changes in layer spacing, layer index and layer modulus. Our plans also include exploiting memory effects of photonic/phononic gels in response to the external stimuli such as pH.

Fabrication of Quasi-Amorphous Structures via Self Assembly of Colloidal Nanoparticles

Quasi-amorphous structures are fascinating in the fields of photonics and phononics due to their favorable isotropic nature for opening complete band gaps. In recent years, some theoretical simulations showed that quasi-amorphous systems possess sizable 3D photonic band gaps. For example, Edagawa et al. [6] recently reported theoretical results on a photonic amorphous diamond (that is a structure with only local tetrahedral ordering of the spheres) structure having a 3D photonic band gap. Jin et al. [7] theoretically demonstrated that 2D quasi-amorphous colloidal particle arrays also exhibit omni-directional photonic band gaps. While crystalline structures from self-assembly of colloidal nanoparticles and their photonic/phononic properties were quite extensively investigated, there are very few examples on *quasi-amorphous* photonic/phononic structures assembled from colloidal nanoparticles due to the difficulty of fabricating amorphous structures having minimal short-range order but without long-range order. In many cases, the colloidal fluid tends to crystallize with moderately long-range order (although it is not a defect free perfect crystal) rather than forming a quasi-amorphous structure with short-range order.

To form quasi-amorphous structures in colloidal particle systems, one needs suppression of crystallization and freezing in of the structure below the glass transition. Cohen and Turnbull [8] suggested that rapidly compressing an assembly of hard sphere could bypass crystallization and should result in a metastable, amorphous glass state. Pusey and van Megan [9] also report on suspensions of colloidal particles that interact via a steep repulsive potential and observed both the freezing transition and, at higher concentrations, glass formation. More recently, Watannabe et al. [10] reported on glassy photonic colloidal array in ionic liquid which effectively suppressed the crystallization by strong ionic repulsions.

We will explore fabrication methods for fabrication of quasi-amorphous photonic band gap materials by taking advantage of crystallization suppression process in colloidal fluid transition. This involves the investigation of the optimized condition for forming stable quasi-amorphous structures with variation of the crystallization suppression parameters. The crystallization in colloidal fluid is known to be very sensitive to solvent, polydispersity of particles, concentration and surface charge. For this work, we are going to use SiO₂ and TiO₂ nanoparticles as model systems due to their versatile accessibility in synthesis and surface modification. Unlike crystalline colloidal structures, the resultant quasi-amorphous structures are expected to still retain fluidic characters, so thereby they would be sensitive to the external stimuli as similar to our previous periodic photonic gel systems (*tunable!!*). These tunable quasi-amorphous structures will be subjected to the investigation of their optical and acoustic properties in response to the various chemical and electrical stimuli.

Modeling 2D and 3D Structures having Dual Band Gaps

The design of 1, 2 and 3D structures which are simultaneously photonic and phononic band gap structures enables research on the possibility of dual acousto-optical band gaps and the simultaneous localization of photons and phonons to greatly enhance phonon-photon interactions. Phononic band structure calculations have been performed using various methods, but only a few types of structures have been examined as compared to the much larger effort in photonic crystals. There are only a handful of experimental studies, most of which dealt with measuring the transmission coefficients for *sonic* (frequency range 20 Hz to 20 kHz) and *ultrasonic* (frequency range 20 kHz to 100 MHz) acoustic waves propagating through a periodic medium. We will focus on a combined theoretical - experimental investigation of visible light photonic crystals - *hypersonic* phononic crystals (frequency range 1-100 GHz).

In order to increase the possibility of simultaneous gaps we needed to make a judicious choice of material systems and length scales for each structure. Since the performance of a photonic crystal depends on the dielectric contrast between the materials, a favorable choice for photonics is a composite made of a high dielectric solid material and air. This solid-air choice also promotes the likelihood of a *phononic* gap due to the large impedance contrast. We used the finite element method to overcome numerical difficulties and were the first to demonstrate the existence of solid-air architectures that display simultaneous complete phononic and photonic gaps (see figure 4).

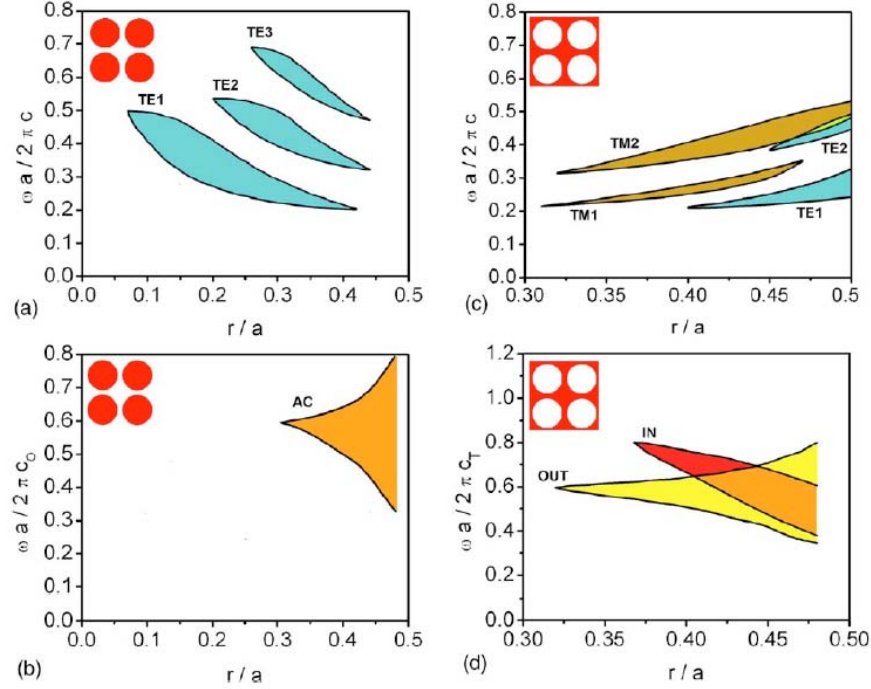


Figure 4. Photonic and phononic band gaps for a perfect array of cylinders in a square lattice of length a . The solid material (red) is assumed to be silicon. (a) Photonic gaps for solid cylinders in air background. (b) Phononic gaps for solid cylinders in air background. Reference [11].

Both self assembly and IL are experimental methods for fabrication of dual band gap crystals. These processing approaches will provide access to wide range of periodic structures with various lattice parameters, unit cell symmetries and material properties as previously mentioned. We will initially concentrate on simpler 1D and 2D systems and BLS will be used to directly measure phononic band diagrams. From a practical perspective, it is crucial to identify easy-to-fabricate structures with the desirable phonon-photon dispersion relation features, mainly large and complete band gaps for both types of waves. A key attribute is the size of the gap - the ratio of the gap width to the midgap frequency.

$$\xi = \frac{\Delta\omega_g}{\omega_{mg}}$$

This ratio depends on the dielectric contrast for light waves and on the differences in sound velocities and densities of the constitutive materials for elastic waves: for photons, the band gap depends only on the dielectric contrast (ϵ_2/ϵ_1) and f , where f is the volume fraction of one of the components; for phonons, one must consider a larger number of parameters: $\rho_1, \rho_2, C_{T1}, C_{T2}, C_{L1}, C_{L2}, C_{T0}$, and f , where C_{T0} is the transverse speed of sound within the medium from which the phonons impinge upon the structure. An organized study is thus needed in order to systematically investigate the dispersion relations for light and elastic waves. The elastic wave equation reveals that band

structures and related frequencies depend on the density ratio ρ_2/ρ_1 . Further, the band structure frequencies can be normalized with respect to, for example, the transverse sound velocity C_{T1} of component 1. As a result, the number of parameters for a systematic study is reduced from eight to six: ρ_2/ρ_1 , C_{T2}/C_{T1} , C_{L1}/C_{T1} , C_{L2}/C_{T1} , C_{T0}/C_{T1} , and f . The mass density contrast required for large phononic band gaps is easily fulfilled with polymer-air structures ($\rho_{\text{polymer}}/\rho_{\text{air}} \sim 10^3$), this reduces the need for further pattern transfer into other materials systems. One advantage of polymeric based systems is the ability to tune the structure, by stretching, swelling, heating etc. Tunable phononic systems are attractive from many design perspectives, for example, they could allow for resonators with tunable ranges of operation. Previously we used mechanical forces to tune a 3D PDMS solid/air phononic crystal.[12]

To realize the full potential of dual photonic-phononic, ie. “phoxonic” crystals one must be able to create structures with each type of dispersion relation tailored to the particular application. To achieve this goal it is necessary (1) to understand the influence of structure, symmetry and materials properties on the features of the phoxonic band diagrams and (2) to identify easy-to-fabricate structures with large phoxonic dual band gaps. Moreover, it is important to realize that in order to strongly couple the two types of waves, we need to localize them in the same place at the same time and to provide waves with comparable energies, hence we need a defect cavity within a hierarchical phoxonic crystal that co-localizes photons and phonons having very different wavelengths – relatively large photon wavelengths (say 600nm) with phonons of relatively small wavelengths (say 6nm). We plan to approach this task by first making a 1D structure within a structure and then fabricating a 2D structure within a structure. For the 1D case, the hierarchical lamellar structures can be created by incorporating crosslinked lamellae with relatively small domain size between swellable photonic gel layers. This can be achieved by sequentially spin coating two distinctive block copolymers- one with low molecular weight and crosslinkable and the other is with high molecular weight and swellable. In this case, the crosslinked lamellae with the smaller domain will serve as a 1D defect layer for both photons and phonons. For the more complex 2D case, we will use a combination of an e-beam patterned template, interference lithography and self assembly to create a BCP, epoxy polymer and air structure with well controlled structures on the two different length scales. Figure 5 shows the idea, whereby we use e-beam patterning to form a template for self assembly of a hexagonal cylinder – forming BCP and the superlattice of a hexagonal air cylinder lattice formed by use of multi-exposure using a simple Llyolds mirror to create sets of interference fringes with 120 degree rotations between the 3 exposures. Then we would create a cavity within a cavity structure to co-localize the two types of waves.

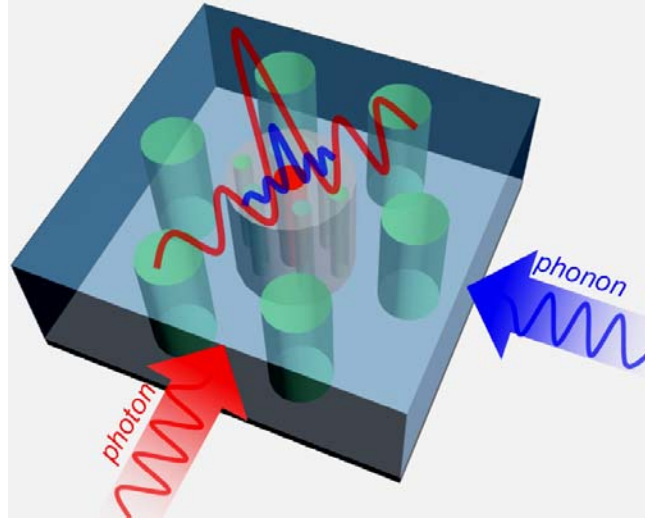


Figure 5. Schematic of a portion of a 2D hierarchical phoxonic crystal with both large scale photonic lattice and a smaller scale phononic lattice inside a cavity resonator in the larger scale lattice.

Acousto-optical Interactions in Dual Band Gap PhoXonic Crystals

There are two factors that determine the strength of acousto-optical interactions: (1) efficiency of coupling between elastic and electro-magnetic fields and (2) the intensities of these fields. The coupling efficiency depends on the microscopic details of both fields. Our FEM calculations have shown that elastic waves in periodic structures are generally mixed waves with complex displacement fields. This modification leads to the enhancement of acousto-optical coupling efficiency for some modes and the suppression for the others. The magnitude of the displacement fields can also be significantly altered in periodic structures. Indeed, no light or mechanical waves are allowed to propagate within photonic or phononic band gaps, respectively. Furthermore, large local intensities of both electro-magnetic and elastic fields can be achieved using defect cavities such as we show in figure 5. The scattering of standing-wave photons from standing-wave phonons by placing an acoustic cavity inside an optical cavity, carefully positioning the acoustic cavity at the peak of the optical amplitude to maximize the strength of the interaction has been recently demonstrated[13]. In a 1D periodic phoxonic structure, by choosing the proper thicknesses for the periodic layers and the cavities, it is possible to create a defect mode within a photonic band gap that corresponds to the wavelength of interest. If a laser beam at this wavelength is focused into the crystal, its electro-magnetic field will be largely localized in the cavity. Similarly, the presence of a corresponding cavity in the smaller scale 1D phononic lattice will lead to significant increase in the population of a certain set of phonons. As a result, we can expect several orders of magnitude increase in the photon-phonon scattering efficiency. This will result in strongly nonlinear behavior of the acousto-optical cavity and can be explored to design novel acousto-optical devices. BLS signal strength will be a direct probe of this effect and by changing the epoxy lattice and the BCP lattice by swelling/deswelling, we can dynamically tune the interaction.

Tunable PhoXonic Band Gap Materials from Self Assembly of Block Copolymers and Colloidal Nanocrystals

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This project initiated in the Fall of 2010 and aims to design and fabricate tunable phoXonic (phoNonic and photonic) band gap materials by self assembly of block copolymers (BCP) and colloids. We also want to characterize both the structures and the resultant properties and critically compare with simulations.

Hanyang Activities:

Hysteric Tunable Photonic Gels and Their Applications

Photonic band gap (PBG) materials have been of great interest due to their potential applications in science and technology. Their applications can be further extended when the PBG becomes tunable against various chemical and electrical stimuli. Recently, it was found that tunable photonic band gap materials can be achieved by incorporating stimuli-responsive smart gels into PBG materials. For example, the characteristic volume phase transition of gels in response to the various external stimuli including temperature, pH, ionic strength, solvent compositions and electric field can be combined with the unique optical properties of photonic crystals to form unprecedented highly responsive optical components. These responsive photonic crystals have been considered as a good platform for actuators, optical switches or displays. Our efforts at Hanyang have focused on tunable PBG materials self-assembled from polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) block copolymers or quasi amorphous colloidal nanoparticles. We demonstrated that selective swelling of lamellar structure is useful for fabricating PBG materials with extremely large tunability. Interestingly, we found strong optical hysteresis in photonic gels, which can be modulated by ion pairing affinity. We also explored the electrophoretic assembly of quasi amorphous colloidal nanoparticles and their applications towards full color display pixels with angular independency. Future work will emphasize quasi amorphous structures and characterization.

MIT Activities

Response Kinetics of Photonic Crystals

The time dependent response of the reflected color from a 1D periodic lamellar BCP stack turns out to depend critically on the defect density in the multilayer film. The time to go from the dry state to the equilibrium swollen state depends on the nature and number of defects (such as screw dislocations) within the film which is a strong function of the processing history of the sample. For example with a BCP of fixed molecular weight (and hence equilibrium dry period), the apparent “equilibrium” swollen period is strongly dependent on the processing conditions. Samples can swell rapidly (within sec) but reach a relatively low swollen period while other samples swell much less rapidly but

swell to a much greater final extent. This unusual behavior can be explained due to the variation of the number of defects in the 2 samples – a system with a large number of defects swells quickly but because the defects form a network (the analogy is that of a more tightly crosslinked rubber), the swelling is less than a sample with few defects that takes longer to swell but swells to a much greater extent. In order for our team to be able to precisely understand structure – stimulant relations, we need to better control the defect density of our samples.

GISAXS – Recently we conducted grazing incidence small angle x-ray scattering measurements during swelling of low molecular weight PS-P2VP polymers at the Cornell High Energy Synchrotron Source (CHESS). The evolution of the Bragg peak with swelling could be recorded at intervals of approximately 1 sec resolution.

Cryo-SEM - We have just achieved our first cross sectional images of frozen-solvent swollen PS-P2VP photonic lamellae via a collaboration at the Technion, Haifa Israel. This technique enables us to view the swollen state of samples in situ.

Thomas is transitioning to Rice University and a new Brillouin Light Scattering apparatus is being ordered for phoNonic characterization of colloidal crystals that are being made in Professor Kang's lab at Hanyang. Joint work on the design and fundamental understanding and hence control of the dispersion relation $w(k)$ for phononic crystals is underway.

Two Photon Fabrication of PhoXonic Crystal Template

The MIT group has recently developed capabilities in two photon direct write lithography (TPDWL). We are aiming to create micron scale templates in order to direct the self assembly of deep sub-micron scale BCPs and/or nanocolloidal particles for the creation of phoXonic crystals where the appropriate length scale of the photonic crystal lies in the micron regime and the phononic crystal is in the nm regime in order to most strongly couple phonon-photon interactions.

Joint Activities

The two co-PIs met in Honolulu, Hawaii in December at the Pacificchem Conference. This enabled a good face to face discussion of on-going and upcoming research directions. Since this meeting Professors Kang and Thomas have discussed student visits but due to the impending move of the Thomas group to Rice University, this exchange will be delayed until the early 2012 when the Thomas labs should be fully functional in the Smalley Institute for Nanotechnology in Houston, Texas.

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